

Nucleophilic Substitution Reactions of Haloarenes

The Core Defensive Mechanisms



Resonance Effect

Hybridisation Difference

Phenyl Cation Instability

Four Shields of Stability: Why Haloarenes Resist Attack



1. Resonance

Electron pairs on the halogen conjugate with the ring's pi-electrons. The C-X bond acquires partial double bond character, making cleavage exceptionally difficult.



2. Hybridisation

The halogen is attached to an sp^2 -hybridised carbon (greater s-character, more electronegative) vs sp^3 in haloalkanes.



3. Phenyl Cation Instability

Self-ionisation produces a phenyl cation that is NOT stabilised by resonance. This completely rules out the $SN1$ mechanism.



4. Electronic Repulsion

The electron-rich benzene ring actively repels approaching electron-rich nucleophiles.



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$$E=mc^2$$



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Measuring the Walls: Hybridisation & Bond Length



Greater **s-character** in the sp^2 carbon holds the electron pair tighter.
Shorter bond = Stronger bond.

Breaching the Fortress: Brute Force Conditions

Chlorobenzene + NaOH

623 K / 300 atm

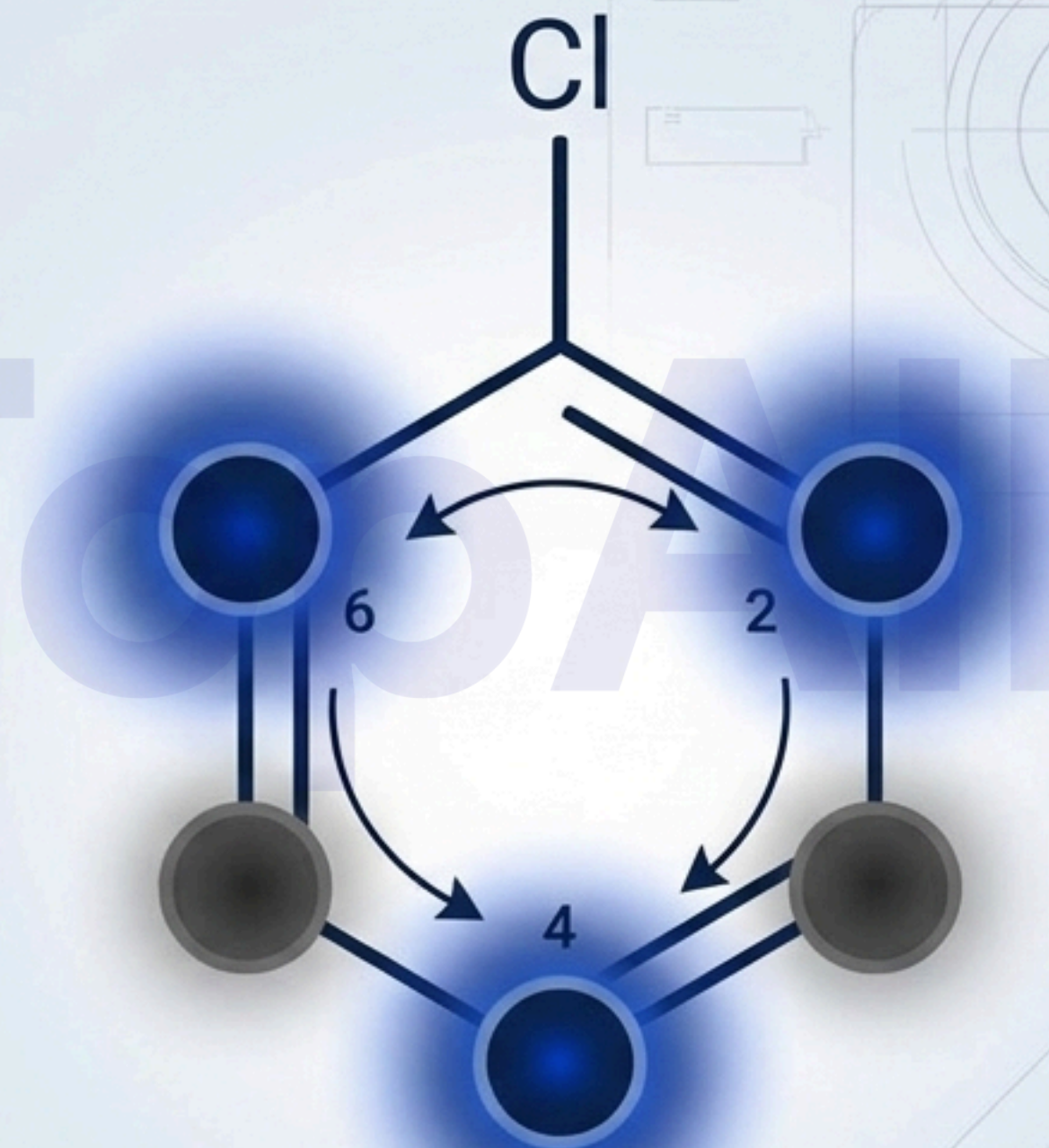


Phenol + NaCl

The Inside Agents:

-NO₂ Position Selectivity

Electron-withdrawing groups like -NO₂ **lower** the fortress defenses by stabilizing the **intermediate carbanion** through **resonance**, but they only have access to specific gates.



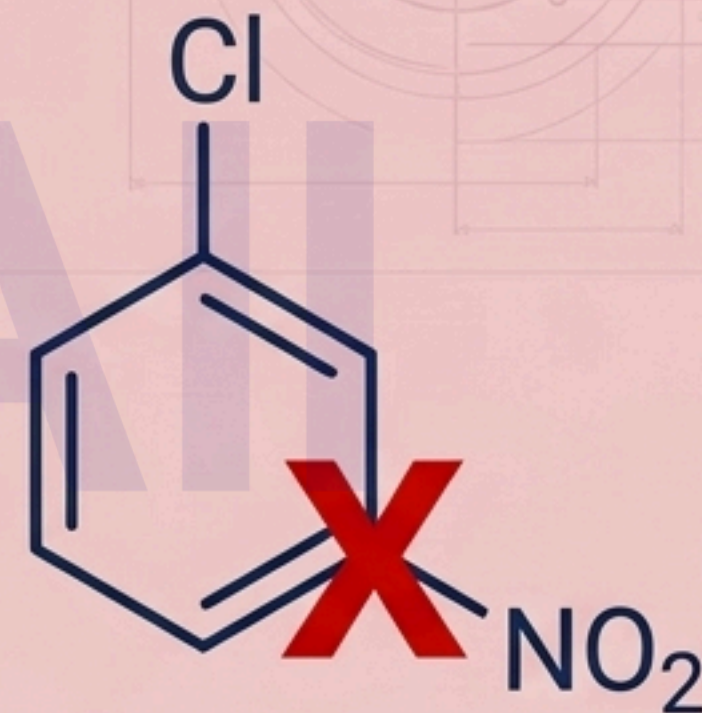
JEE Trap Alert: The Meta Misconception

Watch for this:

The -NO_2 group's activation is strictly position-specific.

Placing an electron-withdrawing group at the meta position offers **NO** stability to the intermediate carbanion. None of the resonating structures place the negative charge on the carbon bearing the -NO_2 group.

Therefore, a meta-substitution provides zero activation for nucleophilic substitution.



Final Intelligence Brief



- Haloarenes heavily resist nucleophiles due to resonance, shorter sp^2 bonds (169 pm vs 177 pm), phenyl cation instability, and electronic repulsion.
- Without activators, forcing substitution requires extreme brute force (623 K / 300 atm).
- $-NO_2$ groups activate the ring towards nucleophiles exclusively at the ortho and para positions by stabilizing the intermediate carbanion.



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